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(54) Title: HIGH TEMPERATURE, LOW VISCOSITY THERMOPLASTIC ELASTOMER BLOCK COPOLYMER COMPOSITIONS

## (57) Abstract

The present invention provides high service temperature, low viscosity rubber compounds and hot melt adhesive and/or sealant compositions by combining from 2 to 30 % by weight of a polyphenylene ether resin having an I.V. of 0.07 to 0.25 deciliters per gram (dl/g) with from 70 to 98 % by weight of an asymmetric radial elastomeric vinyl aromatic hydrocarbon/conjugated diene block copolymer having one of the following formulae: (I)  $(A-HD)_x-Y-(UD)_z$  or (II)  $(UD-A-HD)_x-Y$  or (III)  $(UD-A-HD)_x-Y-(UD)_z$ , wherein A is a vinyl aromatic hydrocarbon block having a weight average molecular weight of from 4,000 to 16,000, HD is a hydrogenated conjugated diene block having a weight average molecular weight of from 10,000 to 50,000, Y is a multifunctional coupling agent, UD is a partially hydrogenated conjugated diene block having a weight average molecular weight of from 1,000 to 45,000, x is an integer from 2 to 30, z is an integer from 1 to 20, and the total of  $x + z$  ranges from 3 to 31. These compositions may be used in adhesive and sealant compositions by adding to them a tackifying resin, typically in an amount from 20 to 400 parts per 100 parts of copolymer. The adhesive and sealant compositions may also contain resins which extend the diene phase, resins which reinforce and/or extend the vinyl aromatic phase, polyolefins, fillers, wax, stabilizers and reactive components designed to crosslink the polymers and/or resins.

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HIGH TEMPERATURE, LOW VISCOSITY THERMOPLASTIC  
ELASTOMER BLOCK COPOLYMER COMPOSITIONS

The present invention relates to high service temperature low viscosity block copolymers which contain polyphenylene ether resins and block copolymers of vinyl aromatic hydrocarbons and conjugated dienes. More particularly, the present invention relates to improved high service temperature block copolymer blends which can be used for rubber compounds and hot melt adhesive and sealant compositions utilizing polyphenylene ether resins and radial elastomeric block copolymers which have both saturated and partially unsaturated diene block arms.

Polyphenylene ether, or PPE, have long been known to enhance the service temperature of vinyl aromatic, usually styrenic, block copolymers. (For convenience, unless otherwise noted, PPE and PS will be used as a shortcut designation for polyphenylene ethers and polyvinyl aromatic hydrocarbon polymers, respectively.). This benefit stems from the thermodynamic compatibility of PPE and PS, the polymer which makes up the hard phase blocks of poly(vinyl aromatic) block copolymers. Being compatible with PS, PPE causes blends of these two polymers to have glass transition temperatures (Tg's) well above that of PS alone and therefore elevates the useful service temperature of block copolymers containing it. Service temperature enhancements of 10 to 60°C above that of the host poly(vinyl aromatic) block polymer (e.g., from 100°C up to 110-160°C) are of commercial interest. PPE, with a Tg of about 215°C, is well able to provide such enhancements.

Unfortunately, the Tg increase afforded by PPE

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comes with a penalty in viscosity. Often the potential benefit of PPE cannot be realized in practical compositions because of this factor. The high viscosity creates difficult mixing, high temperature during mixing, and poor dispersion of PPE in the host polymer. A significant proportion of the PPE never diffuses into the domains of PS where its influence on Tg can be effected. Rather, it remains as a dispersed phase in the rubber, acting like a filler and causing a high viscosity in the final blend.

It is known from WO 90/14397 that low molecular weight grades of PPE reduce the viscosity penalty described above. These grades have intrinsic viscosities (I.V.'s) of about 0.07 dl/g to about 0.25 dl/g, compared to 0.29 dl/g to 0.49 dl/g for commercial grades which exhibit difficult processability. The molecular weight ranges corresponding to the I.V.'s of the latter grades are about 12,000 to 23,000 (Mn) and 30,000 to 60,000 (Mw), respectively.

We have found that, in addition to improved processability, low I.V. PPE grades enhance heat resistance more efficiently than commercial grades.

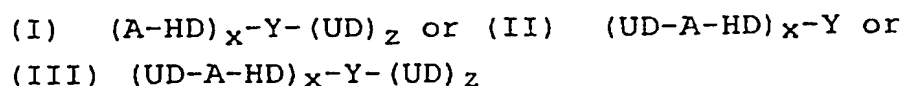
However, there is still a need for improvement in this field. In particular, it would be desirable to be able to provide high service temperature, low viscosity thermoplastic elastomer compositions, containing only a minimum quantity of PPE. Accordingly, it would be desirable to be able to provide thermoplastic elastomer compositions where the increase in slump temperature per weight percent PPE is high, or, preferably and, where the increase in shear adhesion failure temperature (SAFT) per weight percent PPE is high.

Suprisingly, such compositions have now been found.

Therefore, the present invention provides high service temperature, low viscosity rubber compounds and

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hot melt adhesive and/or sealant compositions by combining from 2.0 to 30.0% by weight of a polyphenylene ether resin having an I.V. of 0.07 to 0.25 deciliters per gram (dl/g) with from 70.0 to 98.0% by weight of an asymmetric radial elastomeric vinyl aromatic hydrocarbon/conjugated diene block copolymer having one of the following formulae:



wherein A is a vinyl aromatic hydrocarbon block having a weight average molecular weight of from 4000 to 16,000, HD is a hydrogenated conjugated diene block having a weight average molecular weight of from 10,000 to 50,000, Y is a multifunctional coupling agent, UD is a partially hydrogenated conjugated diene block having a weight average molecular weight of from 1000 to 45,000, x is an integer from 2 to 30, z is an integer from 1 to 20, and the total of x + z ranges from 3 to 31.

According to a preferred embodiment of the invention most surprisingly thermoplastic elastomer compositions have been found where not only the increase in slump temperature and/or SAFT per weight percent PPE is high, but also where the addition of PPE has little influence on the melt viscosity.

In particular, a combination of a low I.V. PPE and a certain class of vinyl aromatic hydrocarbon/-conjugated diene block copolymers has been found wherein the melt viscosity increase is extraordinarily small and for all practical purposes, virtually absent. For example, increases in slump temperatures in a sealant formulation of 30 to 35°C can be obtained with viscosity increases of only 0.3 to 0.4 Pa-sec. The ratio of slump temperature benefit to viscosity increase, i.e., 35°C divided by 0.32 Pa-sec, is 109.

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The corresponding calculation for conventional block copolymer combined with commercial PPE is 30°C divided by 3.11 Pa-sec, or 9.6. Even conventional block copolymer combined with low molecular weight PPE shows only a modest increase in this ratio, i.e., to 10.7. Thus, according to this preferred embodiment, the invention relates to a particular combination of PPE and block copolymer which exhibits unexpected, useful behavior with essentially no reduction in other desirable properties.

Therefore, preferably, the asymmetric radial elastomeric block copolymer has a vinyl aromatic hydrocarbon block having a weight average molecular weight of from 4,000 to 10,000.

According to another preferred embodiment, the asymmetric radial elastomeric block copolymer has a total weight average molecular weight of less than 120,000, preferably less than 115,000, more preferably in the range from 29,000 to 110,000.

According to a particularly preferred embodiment the asymmetric radial elastomeric block copolymer has a total weight average molecular weight and a vinyl aromatic hydrocarbon block molecular weight in the ranges given above.

The compositions of the invention may be used in adhesive and sealant compositions by adding to them a tackifying resin, typically in an amount from 20 to 400 parts by weight per 100 parts of copolymer. The adhesive and sealant compositions may also contain resins which extend the diene phase, resins which reinforce and/or extend the vinyl aromatic phase, polyolefins, fillers, wax, stabilizers and reactive components designed to crosslink the polymers and/or resins.

The first of the primary novel components of the

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compositions of the present invention is the above-described block copolymer which has both saturated and unsaturated arms. Without wishing to be bound by a particular theory, it would appear that the vinyl aromatic-hydrogenated diene arms provide the primary load bearing capability for the intended uses, i.e., adhesive and sealant compositions. It is important that these arms be hydrogenated so that the structural integrity of the polymer is preserved even if outside forces cause degradation of the unsaturated side chains. The unsaturated diene homopolymer arms are important in the composition to give the composition sufficient tack properties and/or the ability to be tackified to make effective compositions, such as pressure sensitive adhesive compositions.

The molecular weights of linear polymers or unassembled linear segments of polymers such as mono-, di-, triblock, etc., or the arms of star polymers before coupling are conveniently measured by Gel Permeation Chromatography (GPC), where the GPC system has been appropriately calibrated. For anionically polymerized linear polymers, the polymer is essentially monodisperse (weight average molecular weight/number average molecular weight ratio approaches unity), and it is both convenient and adequately descriptive to report the "peak" molecular weight of the narrow molecular weight distribution observed. Usually, the peak value is between the number and the weight average. The peak molecular weight is the molecular weight of the main species shown on the chromatograph. For polydisperse polymers the weight average molecular weight should be calculated from the chromatograph and used. The materials used in the columns of the GPC are styrene-divinyl benzene gels or silica gels. The solvent is tetrahydrofuran and the detector is a

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refractive index detector.

5 The polymers of this invention may be hydrogenated as disclosed in U.S. Patent Reissue 27,145. The hydrogenation of these polymers and copolymers may be carried out by a variety of well established processes including hydrogenation in the presence of such catalysts as Raney Nickel, noble metals such as platinum, soluble transition metal catalysts and titanium catalysts as in U.S. Patent 5,039,755. The polymers may have different diene blocks and these diene blocks may be selectively hydrogenated as described in U.S. Patent 5,229,464.

15 The A blocks are polymer blocks of a vinyl aromatic hydrocarbon. Preferably, the vinyl aromatic hydrocarbon is styrene. Other examples of useful vinyl aromatic hydrocarbons include alphas-methyl styrene, various alkyl-substituted styrenes, alkoxy-substituted styrenes, vinyl naphthalene, and vinyl toluene. The HD and UD blocks are polymer blocks of conjugated dienes. The preferred diene for the HD blocks is butadiene. Isoprene is preferred for the UD blocks. Other dienes may also be used, examples of which include piperylene, methyl-pentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, and 4,5-diethyl-1,3-octadiene, preferably those conjugated dienes containing 4 to 8 carbon atoms. It is preferred that the conjugated diene employed in the HD block differ from that employed in the UD block, especially in respect to ease of hydrogenation.

25 The diene in the HD block should preferably hydrogenate faster and more completely than the diene in the UD block. The amount of hydrogenation in the unsaturated (UD) blocks after the reaction may be such that the UD blocks are up to 90 percent saturated, i.e. contain at least 10% residual unsaturation. Preferably, at least 50 percent, most preferably from



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50 up to 90 percent of the original unsaturation of the diene in the UD blocks remain after partial hydrogenation. Generally, the melt viscosity of these polymers is lowered when the residual unsaturation is increased. For hot melt adhesives, it is better to have a lower melt viscosity at a given temperature so that the formulation is more easily processable.

The HD blocks may be hydrogenated as generally described in the prior art, preferably so as to reduce at least about 90 percent of any olefinic double bonds in the polymer chains. Suitably at least 50 percent, preferably at least 70 percent, and more preferably at least 90 percent, most preferably at least 95 percent of the original olefinic unsaturation in the HD blocks is hydrogenated.

It will be appreciated that in any case the residual olefinic unsaturation in the UD blocks is higher than the olefinic unsaturation in the HD blocks.

The dienes used in this invention preferably should be those which are largely amorphous at use temperatures (usually 10°C to 40°C) and do not contain excess crystallinity which would interfere with flexibility. For butadiene, e.g., the percent of 1,2 addition should preferably be at least 30 percent to prevent excessive crystallinity after hydrogenation to ethylene-butylene (EB) rubber. Below 30 percent 1,2 addition, polymer crystallinity is very high, giving a stiff polymer which is not desirable for pressure sensitive adhesives or sealants. For pressure sensitive adhesives, more preferably the percent of 1,2 addition is not more than 65 percent. Above 65 percent the T<sub>g</sub> (glass transition temperature) of the polymer is very high, making it difficult to formulate an acceptable pressure sensitive adhesive.

The preferred method for making the block

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5 copolymers of the present invention is basically described in European Patent Application 0,314,256. Therein is disclosed a two-step process for producing asymmetric radial polymers which avoids the problem of the production of the unwanted homopolydiene polymer. The process involves separately polymerizing the monomers to create separately the two different types of arms. Then one set of the polymeric arms is coupled to the coupling agent and when that coupling reaction is complete, the second set of polymer arms is coupled to the coupling agent. This ensures that there will be very little homopolydiene in the final polymer. In the present invention, for example, isoprene arms would be anionically polymerized, and coupled via the coupling agent. Subsequently or in parallel, styrene-butadiene (SB) arms would be anionically polymerized and at least 2 arms then coupled to the isoprene arms via the coupling agent. These unhydrogenated precursors are useful as adhesives and sealants on their own but they suffer the stability problems common to polymers with a high degree of unsaturation (for example, (SB)<sub>2</sub>-Y-I<sub>2</sub>). Subsequently, the coupled polymer is hydrogenated under conditions that preferably hydrogenate the diene of the A-HD arm (or block) only, leaving the diene of the UD arm (or block) essentially unsaturated.

20 In general, the method described is used to prepare asymmetric radial or star polymers with any polymer containing a reactive end group which will react with one or more functional groups contained in the selected coupling agent. The method is particularly suitable for the preparation of asymmetric radial polymers from so-called "living" polymers containing a single terminal metal ion. As is well known in the prior art, "living" polymers are polymers containing at least one active group such as a metal atom bonded directly to a

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carbon atom. "Living" polymers are readily prepared via anionic polymerization. Since the present invention is particularly well suited to the preparation of asymmetric radial polymers using  
5 "living" polymers to form the arms thereof, the invention will be described by reference to such polymers. It will, however, be appreciated that the invention would be equally useful with polymers having different reactive groups so long as the selected  
10 coupling agent contains functional groups which are reactive with the reactive site contained in the polymer.

Living polymers containing a single terminal group are, of course, well known in the prior art. Methods  
15 for preparing such polymers are taught, for example, in U.S. Patents Nos. 3,150,209; 3,496,154; 3,498,960; 4,145,298 and 4,238,202. Methods for preparing block copolymers such as those preferred for use in the method of the present invention are also taught, for  
20 example, in U.S. Patent Nos. 3,231,635; 3,265,765 and 3,322,856.

When the polymer product is a random or tapered copolymer, the monomers are, generally, added at the same time, although the faster reacting monomer may be  
25 added slowly in some cases, while, when the product is a block copolymer, the monomer used to form the separate blocks are added sequentially.

In general, the polymers useful as arms in the asymmetric radial polymers of this invention may be  
30 prepared by contacting the monomer or monomers with an organoalkali metal compound in a suitable solvent. The process may suitably be carried out at a temperature in the range from -150°C to 300°C, preferably at a temperature in the range from 0°C to 100°C.  
35 Particularly effective polymerization initiators are

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organolithium compounds having the general formula:



wherein R is an aliphatic, cycloaliphatic, alkyl-substituted cycloaliphatic, aromatic or alkyl-substituted aromatic hydrocarbon radical having from 1 to 20 carbon atoms.

In general, the living polymers used as arms in the asymmetric radial polymer will be contacted with the coupling agent at a temperature within the range from 0°C to 100°C, and typically at a pressure within the range from 0 bar to 7 bar. The contacting will be maintained until reaction between the arms and the coupling agent is complete or at least substantially completed, generally for a period of time within the range from 1 to 180 minutes.

In general, the polymers useful as arms in the asymmetric radial polymers of this invention will be in solution when contacted with the coupling agent. Suitable solvents include those useful in the solution polymerization of the polymer and include aliphatic, cycloaliphatic, alkyl-substituted cycloaliphatic, aromatic and alkyl-substituted aromatic hydrocarbons, ethers and mixtures thereof. Suitable solvents, then, include aliphatic hydrocarbons such as butane, pentane, hexane, and heptane; cycloaliphatic hydrocarbons such as cyclohexane, and cycloheptane; alkyl-substituted cycloaliphatic hydrocarbons such as methylcyclohexane, and methylcycloheptane; aromatic hydrocarbons such as benzene and alkyl-substituted aromatic hydrocarbons such as toluene, and xylene; and ethers such as tetrahydrofuran, diethylether, and di-n-butyl ether.

Since the polymers useful in making the asymmetric radial polymers of this invention will contain a single terminal reactive group, the polymers used in preparation of the asymmetric radial polymers will be

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retained in solution after preparation without deactivating the reactive (living) site. In general, the coupling agents may be added to a solution of the polymer or a solution of the polymer may be added to the coupling agent.

Any of the coupling agents known in the prior art to be useful in forming a radial polymer by contacting the same with a living polymer may be used in both the method of this invention and the asymmetric radial polymers of this invention. Suitable coupling agents will contain three or more functional groups, preferably three to forty functional groups which will react with the living polymer at the metal-carbon bond.

While the method will improve the relative distribution of different arms in an asymmetric radial polymer having any number of arms, the method is very effective when the coupling agent contains from three to twenty functional groups reactive with the metal-carbon bond of the "living" polymer. Suitable coupling agents then include  $\text{SiX}_4$ ,  $\text{RSiX}_3$ ,  $\text{HSiX}_3$ ,  $\text{X}_3\text{Si-SiX}_3$ ,  $\text{RX}_2\text{Si-(CH}_2\text{)}_x\text{-SiX}_2\text{R}$ ,  $\text{RX}_2\text{Si(CH}_2\text{)}_x\text{-SiX}_2\text{-(CH}_2\text{)}_x\text{-SiX}_2\text{R}$ ,  $\text{X}_3\text{Si-(CH}_2\text{)}_x\text{-SiX}_3$ ,  $\text{RC(SiX}_3\text{)}_3$ ,  $\text{R(CH}_2\text{SiX}_3\text{)}_3$ , and  $\text{C(CH}_2\text{SiX}_3\text{)}_4$  particularly those containing from three to about six functional groups. In the foregoing formulae: each X may, independently, be fluorine, chlorine, bromine, iodine, hydride, alkoxide radicals, and carboxylate radicals, the said alkoxide and carboxylate radicals preferably containing up to 10 carbon atoms, more preferably containing up to 6 carbon atoms, even more preferably containing up to 4 carbon atoms; R is a hydrocarbyl radical having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms; and x is a whole number from 1 to 6.

Particularly useful coupling agents include

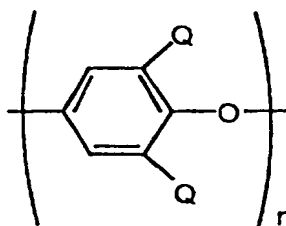
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tetraalkoxysilanes, such as tetramethoxysilane, and the silicon tetrahalides such as silicon tetrafluoride, silicon tetrachloride, silicon tetrabromide and the like, and bis(trihalo)silanes such as bis(trihalo)-silylethane and hexahalodisilane where the halogen may be fluorine, chlorine, bromine, or iodine. Divinylbenzene and oligomers of such are also useful coupling agents.

The coupling process per se is described in detail in U.S. Patent 4,096,203. Specific multifunctional coupling agents useful herein are described in that patent but there are other coupling agents which may also be useful herein, as described above.

The other primary component of the compositions of the present invention is a low molecular weight polyphenylene ether resin (PPE), also known as polyphenylene oxide, having an intrinsic viscosity of 0.07 to 0.25 deciliters per gram (dl/g), when measured in solution in chloroform at 25°C. The PPE may also be described as having 1000 to 15,000 viscosity average molecular weight, 1000 to 10,000 number average molecular weight, or 2000 to 22,000 weight average molecular weight. Typically, these resins have a wider molecular weight distribution than the block copolymers.

The polyphenylene ether resin is preferably one which is comprised of the formula:



wherein the oxygen ether atom of one of the units is connected to the benzene nucleus of the next adjoining

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unit, n is a positive integer and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha carbon atom, halohydrocarbon radicals having at least two carbon atoms between the  
5 halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus.

10 For purposes of the present invention, an especially preferred family of polyphenylene ethers includes those having alkyl substitution in the two positions ortho to the oxygen ether atom, i.e., those of the formula wherein each Q is alkyl, most preferably  
15 having from one to four carbon atoms. The most preferred polyphenylene ether resin for the purposes of this invention is poly(2,6-dimethyl-1,4-phenylene) ether.

20 In general, the polyphenylene ether resins of this invention can be prepared by the following procedures fully described in U.S. Patent Nos. 3,306,874 and 3,257,375.

The polyphenylene ethers are self-condensation products of monohydric monocyclic phenols typically  
25 produced by reacting the phenols in the presence of a complexing agent or complex metal, e.g., copper catalyst. In general, the molecular weight will be controlled by the reaction time with longer times providing a higher average number of repeating  
30 structural units. For low molecular weight PPE, at some point before an intrinsic viscosity of 0.25 deciliters per gram is obtained, the reaction is terminated. Termination can be brought about by the use of conventional means. For instance, in the case of  
35 reaction systems which make use of complex metal

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catalysts, the polymerization reaction can be terminated by adding an acid, e.g., hydrochloric or sulfuric acid, or the like, or a base, e.g., lime, sodium hydroxide, potassium hydroxide, and the like, or the product is separated from the catalyst by filtration, precipitation or other suitable means.

It may be necessary to add an adhesion promoting resin, often referred to as tackifying resin. Typically, a tackifying resin is selected that is compatible with at least the conjugated diene block of the asymmetric radial block copolymer.

A common tackifying resin is a diene-olefin copolymer of piperylene and 2-methyl-2-butene having a softening point of about 95°C. This resin is available commercially under the tradename WINGTACK 95 and is prepared by the cationic polymerization of 60 percent piperylene, 10 percent isoprene, 5 percent cyclopentadiene, 15 percent 2-methyl-2-butene and about 10 percent dimer, as taught in U.S. Patent No. 3,577,398.

Other resins which are also useful in compositions of the present invention include those which are hydrogenated, such as hydrogenated rosins, esters of rosins, polyterpenes, terpene phenol resins and polymerized mixed olefins, lower softening point resins and liquid resins. An example of a liquid resin is Regalrez 1018 resin (a hydrogenated pure monomer resin) from Hercules.

The amount of tackifying resin employed typically varies from 0 to 400 parts by weight per 100 parts of block copolymer (pbw). The selection of the particular tackifying resin is, in large part, dependent upon the specific block copolymer employed in the respective adhesive or sealant composition.

An endblock compatible resin may be included to



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reinforce the vinyl aromatic hydrocarbon portion of the block copolymer. The endblock compatible resin is a resin which is compatible with the polymer block which is normally on the end of the block copolymers of the present invention, i.e., the vinyl aromatic hydrocarbon block. Such endblock compatible resins are often used as reinforcing agents. Normally, these resins should have a ring and ball softening point between 80°C and 150°C although mixtures of aromatic resins having higher and lower softening points may also be used. Preferably, however the average softening point of the mixture is kept between 80°C and 150°C. Useful endblock compatible resins include coumarone-indene resins, poly alpha methyl styrene, polystyrene resins, vinyl toluene-alpha-methyl styrene copolymers and polyindene resins.

Examples of aromatic endblock compatible resins useful in the formulations of the present invention are AMOCO 18 series resins, which are composed of poly alpha methyl styrene (AMOCO); Kristalex series resins, which are composed largely of poly alpha methyl styrene (HERCULES); PICCOTEX Series resins, which are composed of alpha methyl styrene and vinyl toluene (HERCULES); NEVCHEM (NEVILLE) and PICCO 6000 (HERCULES) series resins, which are composed of aromatic hydrocarbons; CUMAR series resins and CUMAR LX-509 (NEVILLE), which are composed of coumarone-indene; PICCOVAR AP series resins (HERCULES), which are composed of alkyl aryl species, PICCOVAR 130 (HERCULES), which is an alkyl aromatic poly indene resin; and ENDEX 155 (HERCULES), a resin derived by copolymerization of pure aromatic monomers.

The compositions of the present invention may contain plasticizers or compounding oils or organic or inorganic pigments and dyes. Optional components are

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stabilizers which inhibit or retard heat degradation, oxidation, skin formation and color formation. Various types of fillers and pigments can be included in the rubber compound or adhesive/sealant formulation. A wide variety of fillers can be used including calcium carbonate, clays, talcs, silica, zinc oxide, and titanium dioxide. Polyolefin resins such as polypropylene, ethylene/propylene copolymers, or copolymers of ethylene/octene or ethylene/hexene can also be used.

The key advantage of the present invention is providing a formulation for an adhesive, sealant, etc. which has a higher service temperature than formulations utilizing the standard block copolymers and high or low viscosity PPE, but does not sacrifice other properties, especially processability.

The addition of the PPE increases the service temperature as well as the viscosity when conventional polymers are used, but when the asymmetric radial polymers of this invention are used, PPE increases the service temperature with little or only a moderate increase in viscosity. The use of these formulations helps to improve the high temperature deformation properties of the thermoplastic elastomers and make them more useful in automotive, wire and cable, and other applications involving high temperatures while also aiding the fabrication processes necessary for these applications. Such applications include sealants, certain types of pressure sensitive tape, contact and structural adhesives, asphalt modification for roofing and paving, thermoplastic modification and fibers.

#### Examples

In the experiments described below, Conventional Polymer 1 is a hydrogenated styrene-butadiene-styrene

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block copolymer with a weight average molecular weight of 83,500, Conventional Polymer 2 is a hydrogenated styrene-butadiene-styrene block copolymer with a weight average molecular weight of 53,000, and Conventional Polymer 3 is an unsaturated styrene-isoprene-styrene block copolymer with a weight average molecular weight of about 150,000. The Invention Polymer is a 4 armed asymmetric radial block copolymer having a weight average molecular weight of 94,000, 2 styrene-hydrogenated butadiene arms having a weight average molecular weight of 34,000, and 2 polyisoprene arms having a weight average molecular weight of about 18,000, wherein 32% of the polyisoprene is hydrogenated.

The endblock reinforcing resin concentration in the formulations of Tables IA and IIA is 13 pbw (parts by weight per hundred parts of the block copolymer) or 3.36% by weight of the whole formulation. The polystyrene concentration of the invention polymer (Table IA) is 18% by weight of the block copolymer and of conventional polymer 1 (Table IIA), 13%. In Table IIIA, the endblock reinforcing resin concentration is 30 pbw or 7.43% by weight of the whole formulation. The polystyrene concentration in conventional polymer 2 in this formulation is 30% by weight. In Table IVA, the endblock reinforcing resin concentration is 22 pbw (7.19 % by weight of the whole formulation) and the polystyrene concentration in conventional polymer 3 in this formulation is 22% by weight.

Several sealant formulations were made with the polymers described above and three PPE's having I.V. of 0.4, 0.15, and 0.115. Temperature dependent properties, such as shear adhesion failure temperature (SAFT) and slump temperature, and melt viscosity were measured. A Brookfield Viscometer model RVTD and

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spindle 29 was used to measure the viscosity at 177°C. To measure the slump temperature, the sealant formulations were poured hot and allowed to solidify in metal channels with the following dimensions: 2.5cm wide, by 2.5cm high, and 1.25cm deep. The channels were placed vertically in an oven and the temperature was raised in 5°C increments, allowing the sample to equilibrate for 30 minutes at each temperature before increasing the temperature again. The slump temperature was the temperature at which the sample sagged more than 0.48 cm (3/16 inch) in the channel. SAFT was determined on a lap-shear bond of 2.5cm x 2.5cm area on an aluminum surface under a load of 160g. The temperature was ramped up from 40°C in 5°C increments every 10 minutes until bond failure occurred.

Table IA  
Sealant Formulation for Invention

Experiment Number	A (Control)	B	1	2
	PBW			
Styrene-ethylene/-butylene-isoprene block copolymer	100.0	100.0	100.0	100.0
PS block reinforcing resin (Endex 155)	13.0	--	--	--
PPE, I.V. 0.40 dl/g	--	13.0	--	--
PPE, I.V. 0.15 dl/g	--	--	13.0	--
PPE, I.V. 0.115 dl/g	--	--	--	13.0
Liquid tackifying resin (Regalrez 1018)	270.0	270.0	270.0	270.0
Antioxidant: Irganox 1010	1.0	1.0	1.0	1.0
UV Stabilizer: Tinuvin 770	1.0	1.0	1.0	1.0
UV Stabilizer: Tinuvin P	1.5	1.5	1.5	1.5
Total PBW	386.5	386.5	386.5	386.5

\* = comparative

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Table IB  
Sealant Properties for Invention

	A	B	1	2
Concentration of PPE, weight percent	-	3.36	3.36	3.36
Slump, °C	50	55	85	80
SAFT, °C	47	51	68	69
Melt Visc. at 177°C, Pa-sec	0.960	1.260	1.280	1.320
Absolute change in melt visc. vs. control, Pa-sec	--	0.300	0.320	0.360
Fractional increase in visc. over control	--	0.313	0.333	0.375
Change in slump vs. control formulation, °C	--	+5	+35	+30
Change in slump per absolute change in visc., °C/Pa-sec	--	17	109	83
Change in slump per fractional increase in visc., °C	--	16	105	80
Change in slump per weight percent PPE, °C	--	1.49	10.4	8.93
Change in SAFT vs. control formulation, °C	--	+4	+21	+22
Change in SAFT per absolute change in visc., °C/Pa-sec	--	13	66	61
Change in SAFT per fractional increase in visc., °C	--	13	64	59
Change in SAFT per weight percent PPE, °C	--	1.2	6.31	6.64

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Table IIA

Sealant Formulation for Conventional Block Polymer 1

Experiment Number	C Control	D	E	F
	PBW			
Styrene-ethylene/butylene block copolymer	100.0	100.0	100.0	100.0
PS block reinforcing resin (Endex 155)	13.0	--	--	--
PPE, I.V. 0.40 dl/g	--	13.0	--	--
PPE, I.V. 0.15 dl/g	--	--	13.0	--
PPE, I.V. 0.112 dl/g	--	--	--	13.0
Liquid tackifying resin (Regalrez 1018)	270.0	270.0	270.0	270.0
Antioxidant: Irganox 1010	1.0	1.0	1.0	1.0
UV Stabilizer: Tinuvin 770	1.0	1.0	1.0	1.0
UV Stabilizer: Tinuvin P	1.5	1.5	1.5	1.5
Total PBW	386.5	386.5	386.5	386.5

Table IIB

Sealant Properties for Conventional Block Polymer 1

	C	D	E	F
Concentration of PPE, weight percent	-	3.36	3.36	3.36
Slump, °C	40	45	55	60
SAFT, °C	36	37	48	50
Melt Visc. at 177°C, Pa-sec	1.07	7.81	7.42	7.05
Absolute change in melt visc. vs. control, Pa-sec	--	6.74	6.36	5.98
Fractional increase in visc. over control	--	6.33	5.97	5.62
Change in slump vs. control formulation, °C	--	+5	+15	+20
Change in slump per absolute change in visc. °. C/Pa-sec	--	0.74	2.36	3.34
Change in slump per fractional increase in visc., °. C	--	0.80	2.5	3.6

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Table IIB (continued)

Change in slump per weight percent PPE, °C	--	1.49	4.46	5.95
Change in SAFT vs. control formulation, °C	--	+1	+12	+14
Change in SAFT per absolute change in visc., °C/Pa-sec	--	0.15	1.89	2.34
Change in SAFT per fractional increase in visc., °C	--	0.16	2.0	2.2
Change in SAFT per weight percent PPE, °C	--	0.30	3.6	4.2

Table IIIA

## Sealant Formulation for Conventional Block Polymer 2

Experiment Number	G Control	H	I	J
	PBW			
Styrene-ethylene/butylene block copolymer	100.0	100.0	100.0	PHR
PS block reinforcing resin (Endex 160)	30.0	--	--	--
PPE, I.V. 0.40 dl/g	--	30.0	--	--
PPE, I.V. 0.15 dl/g	--	--	30.0	--
PPE, I.V. 0.115 dl/g	--	--	--	30.0
Liquid tackifying resin (Regalrez 1018)	270.0	270.0	270.0	270.0
Antioxidant: Irganox 1010	1.0	1.0	1.0	1.0
UV Stabilizer: Tinuvin 770	1.0	1.0	1.0	1.0
UV Stabilizer: Tinuvin P	1.5	1.5	1.5	1.5
Total PBW	403.5	403.5	403.5	403.5

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Table IIIB  
Sealant Properties for Conventional Polymer 2

	G	H	I	J
Concentration of PPE, weight percent	-	7.43	7.43	7.43
Slump, °C	60.0	90.0	105.0	100.0
SAFT, °C	52.2	59.5	81.5	80.0
Melt Visc. at 177°C, Pa-sec	2.04	5.15	6.20	4.63
Absolute change in melt visc. vs. control, Pa-sec	--	3.11	4.20	2.59
Fractional increase in visc. over control	--	1.52	2.06	1.27
Change in slump vs. control formulation, °C	--	30.0	45.0	40.0
Change in slump per absolute change in visc. °C/Pa-sec	--	9.6	10.7	15.4
Change in slump per fractional increase in visc., °C	--	20	22	32
Change in slump per weight percent PPE, °C	--	4.04	6.06	5.38
Change in SAFT vs. control formulation, °C	--	7.3	29.3	27.8
Change in SAFT per absolute change in visc., °C/Pa-sec	--	2.3	7.0	10.7
Change in SAFT per fractional increase in visc., °C	--	4.8	14	22
Change in SAFT per weight percent PPE, °C	--	0.98	3.94	3.74



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Table IVA

Sealant Formulation for Conventional Block Polymer 3

Experiment Number	K Control	L	M
	PBW		
Styrene-isoprene-styrene block copolymer	100.0	100.0	100.0
Processing oil (Shell flex 371)	30.0	30.0	30.0
PS block reinforcing resin (Endex 155)	22.0	--	--
PPE, I.V. 0.15	--	22.0	--
PPE, I.V. 0.115	--	--	22.0
Tackifying resin (Zonatac 105 Lite)	150.0	150.0	150.0
Antioxidant: Irganox 1010	1.0	1.0	1.0
Antioxidant: Polygard HR	0.5	0.5	0.5
UV Stabilizer: Tinuvin 770	1.0	1.0	1.0
UV Stabilizer: Tinuvin P	1.5	1.5	1.5
Total PBW	306.0	306.0	306.0

Table IVB

Sealant Properties for Conventional Polymer 3

	K	L	M
Concentration of PPE, weight percent	--	7.19	7.19
Slump, ° C	85	122.5	115
SAFT, °C	73.2	83.9	93.0
Melt Visc. at 177°C, Pa-sec	23.2	174.0	44.5
Absolute change in melt visc. vs. control, Pa-sec	--	150.8	21.3
Fractional increase in visc. over control	--	6.50	0.92
Change in slump vs. control formulation, °C	--	37.5	30.0
Change in slump per absolute change in visc. °C/Pa-sec	--	0.25	1.4

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Table IVB (continued)

Change in slump per fractional increase in visc., °C	--	5.8	32.6
Change in slump per weight percent PPE, °C	--	5.2	4.2
Change in SAFT vs. control formulation, °C	--	10.7	19.8
Change in SAFT per absolute change in visc., °C/Pa-sec	--	0.071	0.93
Change in SAFT per fractional increase in visc., °C	--	1.64	21.5
Change in SAFT per weight percent PPE, °C	--	1.49	2.75

When one compares the property data for the sealant made with the composition of the present invention shown in Table IB with the properties of the sealants made with the three conventional polymers (Tables IIB, IIIB, and IVB), it is clear that the invention composition is unique in a way that is not shown by the conventional polymer compositions.

The service temperature improvements afforded by the invention polymer 1 are outstanding whether considered as a function of viscosity increase (either absolute or as a fractional increase over the original) or of PPE concentration. For example, the change in slump for formulation 1 (sealant containing invention polymer and 0.15 I.V. PPE) divided by the absolute increase in viscosity gives a figure of 109°C/Pa-sec, compared to only 2.36°C/Pa-sec for the same PPE in conventional polymer 1 (formulation E in Table IIA). Similar figures were obtained when the change in slump was divided by the fractional increase in viscosity (105°C/Pa-sec vs. 2.5°C/Pa-sec).

Taking the SAFT figures as examples in a parallel manner, the invention polymer 1 yielded 66 and 64°C/Pa-sec whereas conventional polymer 1 yielded figures of

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1.89 and 2.0, respectively.

5 The changes in service temperature per unit concentration of PPE in a sealant formulation were also impressive for the invention polymer. Slump increases per unit concentration of PPE in invention polymer formulations were about twice those in conventional polymer formulations, especially for low I.V. PPE's (9 to 10°C vs. 3 to 6°C for conventional polymers 1-3). SAFT increases per unit concentration of PPE in invention polymer formulations were 1.6 to 4.2 times higher than those in conventional polymer formulations.

10 Moreover, the viscosity increase caused by the incorporation of PPE in the invention polymer 1 was much less than that generated by PPE in the conventional polymers. This means that PPE-containing invention polymer processes more easily (e.g., mixes and extrudes with less energy and time) than PPE-containing conventional polymers. In this comparison the viscosity increase is defined as the increase over the control compounds A, C, G and K for Tables IA to IVA, respectively). The control compounds contain conventional endblock reinforcing resin derived from styrenic monomers.

20 Thus, the above experiments demonstrate that the invention composition produces higher service temperatures by a variety of modes of comparison than conventional styrenic block copolymers, ranging from saturated types of different molecular weights and polystyrene contents to typical unsaturated block copolymers in a different formulation.

30 Two further block copolymers (Invention Polymers 2 and 3) were tested for use in sealant formulations according to the invention. Invention polymer 2 is a 4 armed asymmetric radial block copolymer having a weight average molecular weight of 120,100; 2 styrene-

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hydrogenated butadiene arms and 2 polyisoprene arms. The weight average molecular weight of the polystyrene blocks is 11,200 and the polystyrene content is 18.9% by weight. Control sealant formulation N and sealant formulation 3 (experiment 3) were prepared with invention polymer 2.

Invention polymer 3 has the same structure as invention polymer 2, but the total weight average molecular weight is 92,900; the weight average molecular weight of the polystyrene blocks is 9,100 and the polystyrene content is 18.0% by weight. Control sealant formulation O and sealant formulation 4 were prepared with invention polymer 3.

Sealant formulation compositions are reported in Table VA. Properties of the sealant formulation compositions are reported in Table VB.

As can be seen in Table VB, both sealant formulations 3 and 4 show very high increases in slump temperature and SAFT per weight percent PPE. Further, it can be seen that the presence of PPE in formulation 4 has very little influence on the melt viscosity.

Table VA  
Sealant Formulation for Invention Block Polymers

Experiment Number	N Control	3	4	O Control
	PBW			
Styrene-ethylene/butylene block copolymer	100.0	100.0	100.0	100.0
PS block reinforcing resin (Endex 155)	13.0	--	--	13.0
ARIZONA XR-6503	--	26.0	26.0	-
Liquid tackifying resin (Regalrez 1018)	270.0	257	257	270.0
Antioxidant: Irganox 1010	1.0	1.0	1.0	1.0

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Table VA (continued)

UV Stabilizer: Tinuvin 770	1.0	1.0	1.0	1.0
UV Stabilizer: Tinuvin P	1.5	1.5	1.5	1.5
Total PBW	386.5	386.5	386.5	386.5

ARIZONA XR-6503 is a blend of 50% by weight PPE (i.v. 0.115 dl/g) and 50% by weight tackifying resin (styrenated terpene)

Table VB

## Sealant Properties for Invention Block Polymers

	N	3	4	0
Concentration of PPE, weight percent	-	3.36	3.36	-
Slump, °C	80	110	85	55
SAFT, °C	58	77	69	51
Melt Visc. at 177°C, Pa-sec	3.70	8.55	3.14	2.28
Absolute change in melt visc. vs. control, Pa-sec	--	4.85	0.86	-
Fractional increase in visc. over control	--	1.31	0.377	-
Change in slump vs. control formulation, °C	--	+30	+30	-
Change in slump per absolute change in visc., °C/Pa-sec	--	6.19	35	-
Change in slump per fractional increase in visc., °C	--	23	79	-
Change in slump per weight percent PPE, °C	--	8.93	8.93	-
Change in SAFT vs. control formulation, °C	--	+19	+18	-
Change in SAFT per absolute change in visc., °C/Pa-sec	--	3.92	21	-
Change in SAFT per fractional increase in visc., °C	--	14.5	47	-
Change in SAFT per weight percent PPE, °C	--	5.65	5.36	-

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C L A I M S

1. A thermoplastic elastomer composition which comprises:

- 5 (a) from 2.0 to 30.0% by weight of a polyphenylene ether resin having an intrinsic viscosity of 0.07 to 0.25 deciliters per gram, and
- (b) from 70.0 to 98.0% by weight of an asymmetric radial elastomeric vinyl aromatic hydrocarbon/conjugated diene block copolymer having one of the following formulae:

10 (I) (A-HD) $x$ -Y-(UD) $z$  or (II) (UD-A-HD) $x$ -Y or  
(III) (UD-A-HD) $x$ -Y-(UD) $z$

wherein A is a vinyl aromatic hydrocarbon block having a weight average molecular weight of from 4,000 to 16,000, HD is a hydrogenated conjugated diene block  
15 having a weight average molecular weight of from 10,000 to 50,000, Y is a multifunctional coupling agent, UD is a partially hydrogenated conjugated diene block having a weight average molecular weight of from 1000 to 45,000,  $x$  is an integer from 2 to 30,  $z$  is an integer  
20 from 1 to 20, and the total of  $x + z$  ranges from 3 to 31.

2. Thermoplastic elastomer composition as claimed in claim 1, wherein the asymmetric radial block copolymer has a vinyl aromatic hydrocarbon block having a weight  
25 average molecular weight of from 4,000 to 10,000.

3. Thermoplastic elastomer composition as claimed in claim 1 or 2, wherein the asymmetric radial block copolymer has a total weight average molecular weight of less than 115,000.

30 4. Thermoplastic elastomer composition as claimed in any one of claims 1-3, wherein the multifunctional

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coupling agent Y contains from 3 to 20 functional groups.

5      5. Thermoplastic elastomer composition as claimed in any one of claims 1-4, wherein the asymmetric radial block copolymer contains two styrene-hydrogenated butadiene arms and two to four partially hydrogenated or unsaturated polyisoprene arms.

10      6. An adhesive or sealant composition comprising the thermoplastic elastomer composition of any one of the preceding claims and a tackifying resin.

7. Adhesive or sealant composition as claimed in claim 6, wherein the tackifying resin is present in an amount from 20 to 400 parts by weight per 100 parts by weight of asymmetric radial block copolymer.

# INTERNATIONAL SEARCH REPORT

In national Application No  
PCT/EP 97/01558

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L53/02 C08L71/12 C09J153/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 118 748 A (T. FUJITA ET AL.) 2 June 1992	1
A	--- WO 90 14397 A (EXXON CHEM. PAT. INC.) 29 November 1990 cited in the application	1
A	--- US 5 229 464 A (J. ERISKSON ET AL.) 20 July 1993 cited in the application -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No  
PCT/EP 97/01558

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5118748 A	02-06-92	JP 3199256 A	30-08-91
		EP 0389837 A	03-10-90
		JP 3007755 A	14-01-91
-----			
WO 9014397 A	29-11-90	CA 2056374 A	24-11-90
		EP 0473712 A	11-03-92
		JP 4505634 T	01-10-92
		WO 9014396 A	29-11-90
-----			
US 5229464 A	20-07-93	CN 1066275 A	18-11-92
		EP 0516203 A	02-12-92
		JP 5125197 A	21-05-93
		US 5399626 A	21-03-95
		US 5449718 A	12-09-95
-----			

